

PATENT SPECIFICATION

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(54) DRAWN POLYMER ARTICLES

(71) We, METAL BOX LIMITED, of Queens House, Forbury Road, Reading RG1 3JH, Berkshire, a British Company, do hereby declare the invention; for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to drawn polymer articles, and more particularly to processes for the production of oriented polymer articles and the polymer articles produced thereby.

British Patent Specification No. 1,469,526 describes and claims an oriented high density polyethylene polymer material having a weight average molecular weight of less than 200,000; a number average molecular weight of less than 20,000, a ratio of weight average molecular weight \bar{M}_w to number average molecular

weight \bar{M}_n such that for $\bar{M}_n > 10^4$, $\frac{\bar{M}_w}{\bar{M}_n} < 10$

and for $\bar{M}_n \leq 10^4$, $\frac{\bar{M}_w}{\bar{M}_n} < 20$ and a Young's

modulus greater than $3 \times 10^{10} \text{ N/m}^2$. This material is produced by a process in which the polymer is drawn at a temperature and a rate such that the deformation ratio is at least 15.

Polymer materials produced according to British Patent Specification No. 1,469,526 have quite outstanding physical characteristics including an extremely high Young's modulus. However difficulties have been experienced in attenuating such polymer materials in the form of wide sheet or film because the polymer tends to form a "neck" on drawing, that is to say, as the polymer is gradually extended a narrow section of drawn material is formed which gradually increases in length until the polymer is fully drawn. The neck has a considerably smaller cross section than the undrawn material and in particular the width of the drawn material is much less than that of the undrawn material.

It has now been found that the foregoing disadvantage can be substantially mitigated by

inducing drawing of the polymer at a predetermined section of its length subjected to the drawing tension.

According to the present invention there is provided a process for the production of an oriented polymer article which comprises subjecting an elongate orientable polymer article to a longitudinal drawing tension whilst heating a limited area of the polymer article which is subjected to the drawing tension to a temperature below its melting point, the heated area being substantially smaller than the total area which is subjected to the drawing tension and extending transversely across the polymer article, so as to induce drawing preferentially at or adjacent to the heated area, and drawing the polymer article to a draw ratio of more than 10:1, preferably at least 15:1.

Although the invention is generally applicable to the drawing of orientable polymers, it is particularly useful in drawing processes for the production of polymer articles having a high Young's modulus and other outstanding physical characteristics and will henceforth be described in detail in relation to such processes. It is to be understood, however, that the invention is not limited thereto. The invention may be applied to a range of crystallisable or amorphous polymers, but is particularly applicable to vinyl polymers, and more especially to those vinyl polymers that crystallise in a folded chain form, for example linear vinyl hydrocarbon (i.e. 1-olefin) polymers such as polyethylene, polypropylene and ethylene/propylene block copolymers. In this specification a crystallisable polymer is defined as one that is capable of forming a crystalline or semi-crystalline structure on cooling from the melt. The invention may also be applied to other essentially linear organic polymers such as polyethylene oxide, polyoxymethylene and polyacetaldehyde, polyamides such as nylon, polyesters such as terylene and fluorinated polymers such as polytetrafluoroethylene and polychlorotrifluoroethylene. Particularly good results have been obtained with high density polyethylene which in this speci-

fication is defined as a substantially linear homopolymer of ethylene or a copolymer of ethylene containing at least 95% by weight of ethylene, having a density of from 0.91 to 1.0 gms/cm³ as measured by the method of British Standard Specification No. 2782 (1970) method 509B on a sample prepared according to British Standard Specification No. 3412 (1966) Appendix A and annealed according to British Standard Specification No. B(1), such as for example that produced by polymerising ethylene in the presence of a transition metal catalyst.

Preferably the weight average molecular weight (M_w) of the polymer is less than 1,000,000, preferably from 50,000 to 750,000, more preferably 50,000 to 250,000, and the number average molecular weight (M_n) is preferably from 5,000 to 100,000, more preferably 5,000 to 15,000. The molecular weights quoted in this specification are those measured by the gel permeation chromatography method.

The drawing tension must of course be less than the tensile strength of the polymer under the drawing conditions, but sufficient to produce alignment of the molecules by inducing the required plastic deformation over and above any extension which may be produced by flow drawing. A suitable drawing tension may, for example, be within the range from $1 \times 10^4 \text{ N/m}^2$ to $5 \times 10^7 \text{ N/m}^2$, and preferably from $3 \times 10^4 \text{ N/m}^2$ to $1 \times 10^7 \text{ N/m}^2$. The polymer article is drawn to a high draw ratio of more than 10:1 and preferably at least 15:1; in many cases the draw ratio is at least 20:1. In this specification the draw ratio is defined either as the ratio of the final length to the initial length or as the ratio of the cross-sectional areas before and after drawing.

Whilst the polymer article is subjected to the drawing tension a limited area of the polymer article is heated, as described above, to a temperature sufficient to induce drawing preferentially at or adjacent to the heated area.

The temperature must not be so high as to melt the polymer, otherwise orientation will not take place, but it should be sufficient to ensure that drawing takes place at or adjacent to the heated area before the appearance of a neck elsewhere. The optimum temperature depends upon the weight average molecular weight of the polymer and increases with increasing molecular weight. Temperatures within the range of from 60 to 135°C have been found to be suitable, depending on the nature of the polymer, and for a high density polyethylene a temperature within the range of from 80 to 100°C is preferably used. The heated area of the polymer article is preferably from 0.1 to 5.0 cm in length (measured in the direction of drawing) and preferably extends across the full width of the polymer article. The remainder of the polymer article not subjected to the localised heating

is of course kept at a temperature below that of the heated area so that the neck remains in a relatively static position. Preferably the heated area of the polymer article is from $\frac{1}{2}$ to 20%, and most preferably from 1 to 10% of the total area of the polymer article which is subjected to the drawing tension.

The optimum drawing conditions and the speed of drawing depend to some extent upon the nature of the polymer and its previous thermal history. The polymer article may, for example, be drawn between relatively movable clamping means at speeds in excess of 1c per minute, usually around 5 to 20 cm per minute, or between tension rolls at higher speeds of from 30 to 150 cms per minute, up to 2000 cms per minute or more.

The heating means, which is conveniently situated between the relatively movable clamping means or tension rolls, may comprise, for example a heating chamber through which the polymer article may be passed, the chamber being heated by a hot gas or liquid, or a radiant heater or heaters positioned so that the heat is directed on to the limited heated area of the polymer article. Preferably, however, the heating means comprises a heated surface arranged so as to be in contact with a surface of the polymer article. For example, the heating means may comprise a heated tube in contact with the limited area of the polymer article. The tube may be heated internally by a suitable circulating heating fluid. It is found in practice that for continuous drawing processes the longer the polymer article remains in contact with the heated tube the higher will be the draw ratio and thus the Young's modulus. Thus for a given set of drawing conditions, the draw ratio increases with the diameter of the tube and the extent of "wrap-around" of the polymer article around the tube. The diameter of the tube is preferably from about 1 to 10 cms and the extent of wrap-round, expressed as the angle subtended at the centre of the tube is preferably from 20° to 90° depending on the diameter of the tube.

It has been found that oriented polymer articles produced according to the process of the present invention can be made in widths which approximate more closely to the width of the undrawn polymer article than those which have been produced hitherto.

The physical properties of the polymer article can sometimes be further improved by carrying out the drawing process in incremental stages, allowing the polymer to rest between successive stages. The molecular orientation will in most cases be uniaxial, although it is also possible, with an appropriate drawing process, to produce biaxially oriented polymer articles.

The process of the invention may be used to produce elongate oriented polymer articles in the forms for example of tapes, films,

sheets, rods and tubes. It is particularly useful for the production of tapes, films and sheets having a thickness before drawing of less than 1 mm.

5 As mentioned above, the previous thermal history of the polymer affects the optimum drawing conditions, and may also affect the final properties of the polymer article.

10 Although the invention is not limited to any particular theory it is believed that an excessive number of interlamellar molecular chains, that is to say, molecular chains incorporated in more than one crystal lamella, reduces the degree of molecular orientation and alignment obtainable upon drawing due to an increase in the number of permanent physical entanglements, and consequently prevents the attainment of the optimum physical properties. It may be desirable therefore to subject the polymer to a thermal treatment having the effect of reducing the probability that an excessive number of molecular chains are incorporated in more than one lamella for example by achieving a molecular weight fractionation in the sense that a substantial fraction of the molecules of intermediate weight are allowed to crystallise in discrete very regularly folded chain lamellae whilst a smaller number of both very high and very low molecular weight molecules separate and in a few cases interconnect the crystalline regions. This effect may be obtained in three ways:

35 1) Cooling the polymer from a temperature at or above its melting point at a predetermined rate to ambient temperature so that the desired crystal structure is obtained. The cooling rate used is dependent upon the molecular weight characteristics of the polymer. Usually it is necessary to cool the polymer at an imposed rate of less than 40°C per minute and preferably less than 20°C per minute.

45 2) Cooling the polymer from a temperature at or above its melting point at a predetermined rate to a temperature below its crystallisation temperature and then quenching the polymer to ambient temperature. The cooling rate is preferably from 1° to 15°C per minute, and most preferably from 2° to 10°C per minute. Preferably the polymer is quenched after reaching a temperature of from 5° to 20°C below its crystallisation temperature. Quenching should preferably be at a rate of less than 100,000°C per minute.

55 3) Rapidly cooling or quenching the polymer from a temperature at or above its melting point to a temperature close to or at its crystallisation temperature and maintaining the polymer at that temperature for a period of time sufficient to allow crystallisation to occur.

60 Preferably the polymer is held at a temperature which is within 15°C of the crystallisation temperature for a period of time of from 0.5 to 10 minutes. Subsequently, the polymer

is preferably quenched to ambient temperature.

The choice of conditions used in methods (1), (2) and (3) will depend upon the molecular weight characteristics of the polymer. In general, however, extremely slow cooling rates (less than 1°C/minute) do not produce a crystal structure suitable for attenuation if the polymer has a particularly narrow molecular weight distribution. Also cooling rates greatly in excess of 40°C/minute for methods (1) and (2) and excessive periods of retention at the crystallisation temperature for method (3) have also been found to be deleterious.

80 An alternative method of producing a crystal structure in which the possibility that a given molecular chain is incorporated in more than one crystal lamella is substantially reduced, comprises cooling the polymer very rapidly from a temperature at or above its melting point to a temperature well below its crystallisation temperature to achieve a comparatively low crystallinity. This method, which will be termed method (4) greatly reduces the size of the spherulites and produces a structure comprising crystallites surrounded by large amorphous regions, thereby reducing the number of inter-lamellar molecular chains. Preferably the cooling rate is in excess of 1,000°C/minute, most preferably in excess of 5,000°C/minute through the crystallisation range, and the polymer is cooled to ambient temperature or below. Depending upon the molecular weight characteristics of the polymer it may be found advantageous to reheat the cooled polymer to increase the size of the crystalline regions before attenuation.

105 The process of the invention is capable, for example, of producing a polyethylene polymer article having a Young's modulus as hereinafter defined well in excess of 3×10^{10} N/m² and in some cases at least 5×10^{10} N/m².

Polymer articles according to the present invention can be produced in the form of coherent unitary structures.

Processes according to the invention will now be described by way of example and with reference to the accompanying drawings, of which:—

Fig. 1 is a diagrammatic side elevation of a drawing device having tension rollers and a heated metal tube;

Fig. 2 is a diagrammatic side elevation showing an air oven;

Fig. 3 is a diagrammatic side elevation showing radiant heaters; and

Fig. 4 shows a length of polymer strip in its drawn and undrawn states.

Fig. 5 illustrates diagrammatically a drawing device of the tensometer type using a heated metal tube.

The device shown in Figure 1, for drawing

a polymer strip 1, comprises a frame, not shown, carrying a set of tensioned rollers 10, a small guide pin or roller 12, and a set of feed rollers 13. Between the guide pin 12 and the rollers 10 there is a fixed transverse metal tube 11 through which hot oil can be circulated continuously at a predetermined temperature by known means (not shown).

The apparatus shown in Figures 2 and 3 illustrate the use of two alternatives to the tube 11, in or associated with apparatus according to Figure 1 or other suitable drawing apparatus for performing the process of the invention. Figure 2 shows a simple air chamber or oven 20 of known type having an inlet 21 and an outlet 22 for polymer strip 1 passing therethrough. Figure 3 shows a pair of opposed radiant heaters 30 of known type, separated by a predetermined gap 31 through which polymer strip 1 can be passed.

The apparatus illustrated in Figure 5 is basically a modified Hounsfield tensometer and comprises clamping jaws 50 and 51 which are mounted through grooved wheels 54 on a pair of horizontal rails 55 (only one of which is shown). The jaw 50 can be adjustably restrained against movement whereas the jaw 51 can be moved horizontally at a controlled speed by rotation of a screw 52 by gearing 56. The polymer strip 1 is gripped by both jaws 50, 51 and passes around a part of the periphery of a heated metal tube 53 with an angle of wrap-around of between 60° and 90°. The tube 53 may be heated by circulating hot oil through it. As the jaw 51 moves away from the jaw 50, the polymer material is drawn from a neck which is formed at the transverse section of the strip which is heated by the tube 53. The neck tends to move back towards the jaw 50 during drawing, so a small compensatory movement of jaw 50 or of tube 53 is provided to ensure that heating is applied to the neck throughout the drawing process.

It will be seen that, in all the apparatus described above, the heating is applied to a limited area of the polymer strip which is substantially smaller than the total area of

the strip which is subjected to the drawing tension.

Figure 4 illustrates the formation of a neck 40 during the passage of the strip 1 through the heating means (for example over the tube 11 or 53 or through the oven 20 or heaters 30) of or associated with the drawing means used in the process of the invention. In Figure 4 the neck defines a junction between "undrawn" and "drawn" portions of the strip 1 (indicated at 41 and 42 respectively), the strip moving in the direction indicated.

In Figures 2 and 3, with the strip moving in the direction indicated therein, the neck 40 will occur for example at the position shown.

The invention is illustrated by the following Examples:

EXAMPLE 1.

This Example describes a process according to the invention using Rigidex 50 (Trade Mark), a high density polyethylene manufactured by B.P. Ltd., having a melt flow index of 5.5, M_n of 6180 and M_w of 101450.

Strips of Rigidex 50, 1.27 cm in width and 0.127 cm thick, are formed by compression moulding in a hot press at 160°C, cooling at 10°C per minute to 110°C and then quenching in water to room temperature. A strip is then placed in the jaws of a Hounsfield tensometer, similar to the apparatus of Figure 5 but having situated between the jaws of the tensometer a container 2.5 cm in depth, for example the oven 20 of Figure 2, which is heated internally by a hot air current at 80°C, and is preferably provided with baffles (not shown) to ensure uniform distribution of the hot air. The strip passes through the slits 21, 22 in the front and rear of the heated container. The jaws of the tensometer, which are initially 15 cm apart, are then activated and the polymer is drawn at a rate of 5 cm per minute for 200 seconds.

For comparison the procedure is repeated with the entire strip surrounded by a heating chamber having a temperature of 80°C. The results are given in Table 1:

TABLE 1

Polymer strip		Drawn width (cm)	strip thickness (cm)	Percentage reduction in width		Draw Ratio
initial width (cm)	initial thickness (cm)					
1.27	0.127	0.686	0.007	46%	13	Heated section 2.5 cm
1.27	0.127	0.280	0.025	78%	23	Strip totally enclosed in heating chamber

From Table 1 it can be seen that the reduction in width on drawing is much less using the process of the invention than with the strip totally enclosed in the heating chamber.

EXAMPLE 2.

The procedure of Example 1 is repeated using the same apparatus, but with polymer strips of varying widths and thicknesses. The temperature of the heated oven 20 is such that the polymer strip is heated to 80°C. The results are given in Table 2:

TABLE 2

Polymer strip		Drawn width (cm)	strip thickness (cm)	Percentage reduction in width	Draw Ratio
initial width (cm)	initial thickness (cm)				
5.0	0.079	3.6	0.0079	28%	14
9.0	0.159	6.2	0.0063	31%	36
10.0	0.159	7.5	0.0081	25%	26

EXAMPLE 3.

The process of Example 1 is repeated, replacing the heated container 20 with a hollow copper tube (such as the tube 53,

Fig. 5) of 3.6 cm diameter, heated internally by oil at 80°C. The tube is arranged so that the angle of wrap-round of the strip is 60°. The results are given in Table 3.

TABLE 3

Polymer strip		Drawn width (cm)	strip thickness (cm)	Percentage reduction in width	Draw Ratio
initial width (cm)	initial thickness (cm)				
8.1	1.02	6.1	.005	25%	24:1

EXAMPLE 4.

Strips of Rigidex 50 prepared by forming, cooling and quenching as described in Example 1 are drawn on a suitable drawing machine such as the device shown in Figure 1, at a speed of 3 metres per minute in the direction

shown by the arrows. The tube 11 which is of steel and is heated by oil at 95°C, has a diameter of 7.6 cm, and is so positioned that the angle of wrap-around of the strip on the tube 11 is 90°C. The results are given in Table 4.

TABLE 4

Polymer Strip		Drawn width (cm)	strip thickness (cm)	Percentage reduction in width	Draw Ratio
initial width (cm)	initial thickness (cm)				
7.6	0.056	4.83	0.0064	20%	15

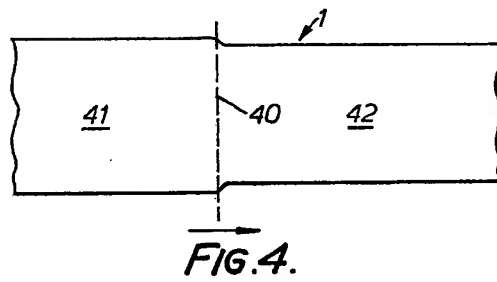
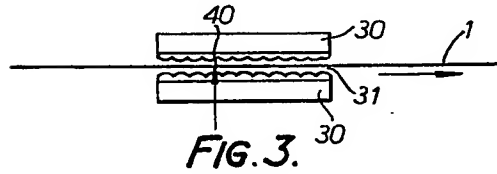
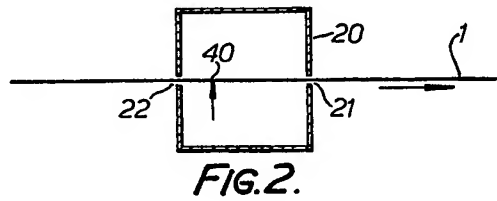
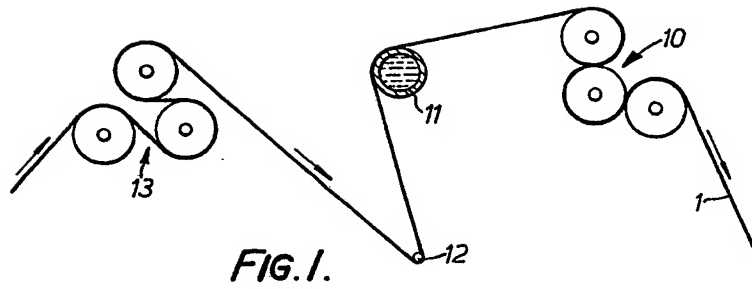
WHAT WE CLAIM IS:—

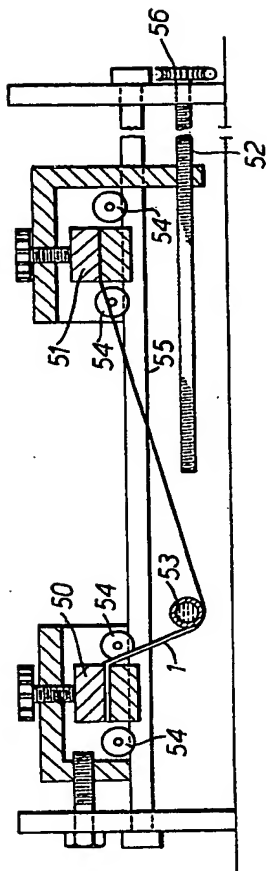
1. A process for the production of an oriented polymer article, which comprises subjecting an elongate orientable polymer article to a longitudinal drawing tension whilst heating a limited area of the polymer article which is subjected to the drawing tension to a temperature below its melting point, the heated area being substantially smaller than the total area which is subjected to the drawing tension and extending transversely across the polymer article, so as to induce drawing preferentially at or adjacent to the heated area, and drawing the polymer article to a draw ratio of more than 10:1.
2. A process according to Claim 1, wherein the polymer article is drawn to a draw ratio of at least 15:1.
3. A process according to Claim 1 or 2, wherein the polymer article is drawn to a draw ratio of at least 20:1.
4. A process according to any one of the preceding Claims, wherein the orientable polymer is a high density polyethylene as herein defined.
5. A process according to any one of the preceding Claims, wherein the weight average molecular weight of the polymer is less than 1,000,000.
6. A process according to Claim 5, wherein the weight average molecular weight of the polymer is from 50,000 to 750,000 and the number average molecular weight is from 5,000 to 100,000.
7. A process according to Claim 6, wherein the weight average molecular weight is from 50,000 to 250,000 and the number average molecular weight is from 5,000 to 15,000.
8. A process according to any one of the preceding Claims, wherein the drawing tension is within the range from $1 \times 10^6 \text{ N/m}^2$ to $5 \times 10^7 \text{ N/m}^2$.
9. A process according to Claim 8, wherein the drawing tension is within the range from $3 \times 10^6 \text{ N/m}^2$ to $1 \times 10^7 \text{ N/m}^2$.
10. A process according to any one of the preceding Claims, wherein the heated area of the polymer article is heated to a temperature within the range from 60°C to 135°C.
11. A process according to Claim 10, wherein the polymer is a high density polyethylene and the temperature used is within the range from 80°C to 100°C.
12. A process according to any one of the preceding Claims, wherein the heated area of the polymer article is from 0.1 to 5.0 cm in length measured in the direction of drawing.
13. A process according to any one of the preceding Claims, wherein the heated area of the polymer article extends across the full width of the polymer article.
14. A process according to any one of the preceding Claims, wherein the heated area of the polymer article is from $\frac{1}{2}$ to 20% of the total area of the polymer article which is subjected to the drawing tension.
15. A process according to Claim 14, wherein the heated area of the polymer article is from 1 to 10% of the total area subjected to the drawing tension.
16. A process according to any one of the preceding Claims, wherein the polymer article is drawn between relatively movable clamping means at a speed in excess of 1 cm per minute.
17. A process according to Claim 16, wherein the polymer article is drawn at a speed of 5 to 20 cm per minute.
18. A process according to any one of Claims 1 to 15, wherein the polymer article is drawn between tension rolls at a speed of 30 to 2000 cm per minute.
19. A process according to Claim 18, wherein the polymer article is drawn at a speed of 30 to 150 cm per minute.
20. A process according to any one of the preceding Claims, wherein the heating is effected by a heated surface in contact with the polymer article.
21. A process according to Claim 20, wherein the heated surface is the surface of a heated tube.
22. A process according to Claim 21, wherein the tube is heated internally by a circulated heating fluid.
23. A process according to Claim 21 or 22, wherein the polymer article is in contact with a section of the periphery of the heated tube which subtends an angle of from 20 to 90° at the centre of the tube, the diameter of the tube being from 1 to 10 cm.
24. A process according to any one of Claims 1 to 19, wherein the heating is effected by passing the polymer article through a heating chamber heated by a hot gas or liquid.

25. A process according to any one of Claims 1 to 19, wherein the heating is effected by a radiant heater or heaters positioned so as to direct heat on to the limited heated area of the polymer article. 5
26. A process according to any one of the preceding Claims, wherein the drawing process is carried out in incremental stages, allowing the polymer to rest between successive stages. 10
27. A process according to Claim 1 for the production of an oriented polymer article, substantially as hereinbefore described with reference to the accompanying drawings. 15
28. Oriented polymer articles produced by the method of any one of the preceding Claims. 15

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